

CRYSCOR: a Public Code for the Post-Hartree-Fock Treatment of Periodic Systems. Supplementary information.

Cesare Pisani,¹ Martin Schütz,² Silvia Casassa,¹ Denis Usvyat,²
Lorenzo Maschio,¹ Marco Lorenz,² and Alessandro Erba¹

¹*Dipartimento di Chimica IFM, and Centre of Excellence NIS (Nanostructured Interfaces and Surfaces),
Università di Torino, via Giuria 5, I-10125 Torino (Italy)*

²*Institute for Physical and Theoretical Chemistry, Universität Regensburg,
Universitätsstrasse 31, D-93040 Regensburg (Germany)*

(Dated: January 20, 2012)

PACS numbers:

In the supplementary material we provide the technical details of the calculations.

Section III.A.

The three layer MgO (100) slab with the experimental Mg-O distance of 2.105 \AA was used to mimic the (100) surface of the MgO crystal. The Gaussian basis sets of type type 10-7111d(2)f(1) for Mg, and 10-6111d(3)f(2) for O were taken from Ref. 2 (BS4). For the SCF calculations³ the TOLINTEG parameters were set to 7 7 7 20 50, and the FMIXING to 40.

In the LMP2 calculations (see Ref. 4 for description of the input syntax) the WF domains \mathcal{D}_i include the PAOs of the O atom (where the WF is centered), and of the five or six neighboring Mg atoms. Electron repulsion integrals of WF pairs with $R_p \leq R_{\text{DF}}^{\text{max}} = 7 \text{ \AA}$ are calculated via density fitting, those with $R_{\text{DF}}^{\text{max}} > R_p \leq R_p^{\text{max}} = 12 \text{ \AA}$ are approximated by multipole expansion. For the density fitting combined Poisson/Gaussian-type PG-AVTZ fitting basis sets, constructed according to procedure described in Ref. 5, were employed. Pair energies of WF pairs with $R_p > R_p^{\text{max}}$ were not explicitly treated at the MP2 level, but evaluated by means of C_6 -extrapolation (the C_6 coefficients were fitted on the fly by using the pair energies of pairs with $8 \text{ \AA} \leq R_p \leq R_p^{\text{max}}$)⁶. Table I compiles the HF and LMP2 correlation energies for calculations with different supercells, along with corresponding supercell parameters.

Section III.B.

The adsorption energy of the argon monolayer on the three layer MgO (100) slab (see above) in the 2×2 arrangement (one Ar atom per $[11\bar{1}1]$ supercell of the MgO slab) was calculated. The counterpoise corrected adsorption energy was computed as the difference between the energy of the Ar-MgO systems (for adsorbate-slab separations of 3.2, 3.4, 3.6, 3.8, 4.0, 4.5, 5.0, and 6.0 \AA), and the energy of the MgO slab with ghost functions on Ar atoms plus the energy of the Ar monolayer with ghost functions on the slab atoms. Additionally, calculations with 1-, 2-, 5-, and 7 layer slabs were also performed.

A pseudopotential in conjunction with an augmented triple-zeta quality basis set (the [ECP4s4p3d1f] basis set A from Ref. 7 plus one set of diffuse f-functions with exponent 0.28 a.u) was used for Argon. The specifications for the HF calculation were: TOLINTEG 7 7 7 25 75 (specified at 3.2 \AA monolayer-slab separation), FMIXING 40, 8×8 k-mesh.

In the LMP2 calculations the PAOs were generated by employing the 8×8 k-mesh. For the Ar-WFs the domains

include the PAOs of this Ar atom. The domains for the WFs of the slab are already described above in section section III.A. If not explicitly specified in the text, the intra-slab pair cutoff radius was set to $R_{\text{p-intra}}^{\text{max}} = 6 \text{ \AA}$, and the inter pair cutoff radius to $R_{\text{p-inter}}^{\text{max}} = 12 \text{ \AA}$. The pair energies from inter-pairs beyond this distance, including those related to semi-infinite slab replicas, were extrapolated by means of the C_6 coefficients, fitted to the inter-pair energies from the range 8-12 \AA . In the calculations involving slabs of different thickness the inter pair cutoff radius was increased to $R_{\text{p-inter}}^{\text{max}} = 14 \text{ \AA}$. Local direct-space fitting⁵ was employed throughout, using Poisson/Gaussian-type AVTZ fitting basis sets⁵. Point group symmetry was exploited; C_{4h}^1 for the on-oxygen and on-Mg adsorption geometries, and C_{2h}^1 for the Mg-Mg bridging position. Due to technical problems during the WFs symmetrization procedure, the 5-layer MgO-Ghost(Ar), and 7-layer MgO-Ar calculations were performed without point group symmetry.

Section IV.A. The rolled and unrolled nanoscroll geometries were optimized at the B3LYP-D2 level with the cc-pVDZ basis set. For this step TOLINTEG 8 8 8 12 30 and the shrinking factor of 8 were set, together with a dense DFT integration grid (XLGRID). The same values were used also for the B3LYP calculations on the optimized geometries. For the Hartree-Fock calculations the same parameters were employed except for the fifth TOLINTEG value, that was set to 40. For the MP2 calculations $R_{\text{DF}}^{\text{max}}$ was set to 6 \AA , and R_p^{max} to 12 \AA . The PG-AVDZ fitting basis was used, and the shrinking factor 16 was set for both the reciprocal space PAO generation and for the localization step. Pair excitation domains were automatically defined by the Boughton-Pulay criterion DOMPUL 0.99.

Section IV.C. The basis set used in the calculations was that from Ref. 8. Other parameters were: TOLINTEG 7 7 7 25 50, shrinking factor 6. The $8 \times 8 \times 8$ k-meshes was used for both the WF and PAO generation. In the LMP2 calculations 4-atom WF domains and the PG-VTZ fitting basis were employed.

Section IV.C. The clathrate from Ref. 9 at its experimental geometry was studied. In the periodic HF calculations (Clathrate, empty Hydrate structure), the following values were set: TOLINTEG 7 7 7 16 60, shrinking factor 4 ; LEVSHIFT 6 1; FMIXING 60. The isolated methane molecule was taken as extracted from

TABLE I: The structural and computational parameters for the HF and LMP2 calculations performed for the three layer MgO (100) slab with different supercells. The resulting total HF and LMP2 correlation energies are reduced to the minimal cell containing six atoms. The number of k-points sampling the Brillouin Zone in the HF, localization, and PAO generation steps are also given.

Supercell	No. of k-points HF/LMP2	No. of atoms per cell	No. of AOs per cell	No. of ij -pairs	HF energy, hartree (per 6-atom cell)	LMP2 energy, hartree (per 6-atom cell)
Symmetry D_{4h}^1						
[1001]	100/64	6	240	447	-824.05836695	-0.84981944
[11 $\bar{1}$ 1]	64/64	12	480	768	-824.05836445	-0.84980280
[2002]	64/36	24	960	1332	-824.05836508	-0.84979628
[2 $\bar{2}$ $\bar{2}$ 2]	36/16	48	1920	2442	-824.05836531	-0.84979484
[3003]	25/16	54	1200	2654	-824.05836534	-0.84979674
[4004]	25/9	96	2160	4572	-824.05836544	-0.84979400
[3 $\bar{3}$ $\bar{3}$ 3]	25/9	108	3840	5112	-824.05836544	-0.84979394
[5005]	25/4	150	4320	6863	-824.05836548	-0.84984748
Symmetry C_1^1						
[1001]	100/64	6	240	3566	-824.05836444	-0.84980682
[11 $\bar{1}$ 1]	64/64	12	480	7132	-824.05836500	-0.84980605
[2112]	64/64	18	720	10698	-824.05836513	-0.84980193
[2002]	64/36	24	960	14264	-824.05836540	-0.84980535
[21 $\bar{1}$ 2]	64/36	30	1200	17830	-824.05836524	-0.84980474
[2 $\bar{2}$ $\bar{2}$ 2]	36/16	48	1920	28528	-824.05836539	-0.84979329

the bulk and surrounded by ghosts with the CRYSTAL keyword MOLEBSSE with distance parameters for the inclusion of ghosts set to 1 4. Localization was performed with the shrinking factor set to 8. The LMP2 calculations were done with the shrinking factor of 4 for the PAO generation, molecular excitation domains, $R_{DF}^{\max} = 6$ Å, $R_p^{\max} = 12$ Å and the PG-AVTZ fitting basis set.

Section VI

The MgO and LiH crystals with the lattice constants of 4.20 Å and 3.99 Å, respectively, were studied. Calculations employed the following parameters: shrinking factor 8, TOLINTEG 7 7 7 20 80, FMIXING 30. The corresponding LDA calculations used VWN as the correlation functional. In the DFT calculations LEVSHIFT 10 0 was used.

In the CIS calculations the $6 \times 6 \times 6$ and $7 \times 7 \times 7$ k-meshes were utilized for MgO and LiH, respectively. In both cases the PG-VDZ fitting was employed.

¹ R. M. Hazen, *Am. Miner.* **61**, 266 (1976).

² R. Martinez-Casado, G. Mallia, D. Usvyat, L. Maschio, S. Casassa, M. Schütz, and N. M. Harrison, *J. Chem. Phys.* **134**, 014706 (2011).

³ R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, K. Doll, N. M. Harrison, B. Civalleri, I. J. Bush, et al., *CRYSTAL09 User's Manual*, Università di Torino, Torino (2010), <http://www.crystal.unito.it>.

⁴ A. Erba and M. Halo, *CRYSCOR09 User's Manual*, Università di Torino, Torino (2010), <http://www.cryscor.unito.it>.

⁵ M. Schütz, D. Usvyat, M. Lorenz, C. Pisani, L. Maschio, S. Casassa, and M. Halo, in *Accurate Condensed Phase*

Quantum Chemistry, edited by F. R. Manby (CRC Press, Boca Raton, FL, 2010), p. 29.

⁶ C. Pisani, L. Maschio, S. Casassa, M. Halo, M. Schütz, and D. Usvyat, *J. Comp. Chem.* **29**, 2113 (2008).

⁷ K. Rościszewski, B. Paulus, P. Fulde, and H. Stoll, *Phys. Rev. B* **60**, 7905 (1999).

⁸ R. Demichelis, B. Civalleri, P. D'Arco, and R. Dovesi, *Int. J. Quantum Chem.* **110**, 406 (2010).

⁹ J. S. Loveday, R. J. Nelmes, M. Guthrie, S. A. Belmonte, D. R. Allan, D. D. Klug, J. S. Tse, and Y. P. Handa, *Nature* **410**, 661 (2001).